



The
Patent
Office

PCT/GB 97/01667

09/202758 5

The Patent Office
Concept House
Cardiff Road
Newport

South Wales

NP9 1RH/EC/1 22 JUL 1997

WIPO

PCT

PRIORITY DOCUMENT

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

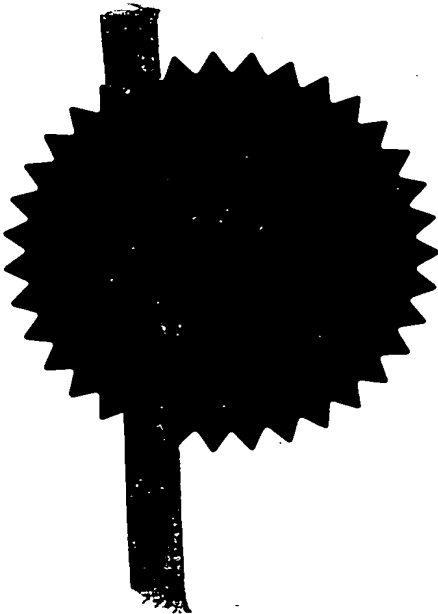
Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.

Signed

Andrew Gersey

Dated

3 July 1997



THIS PAGE BLANK (USPTO)

Patents Form 1/77

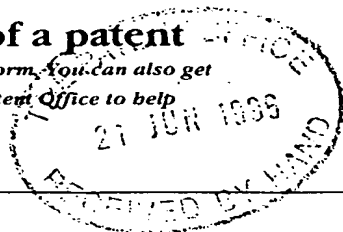
Patents Act 1977
(section 16)

The
**Patent
Office**

23 JUN 96 E202446-1 002826
P01/7700 25.00

Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)



21 JUN 1996

The Patent Office

Cardiff Road
Newport
Gwent NP9 1RH

1. Your reference

BP-08-1054

2. Patent application number

(The Patent Office will fill in this part)

9613023.2

3. Full name, address and postcode of the or of each applicant (underline all surnames)

THE MORGAN CRUCIBLE COMPANY PLC
Morgan House, Madeira Walk,
Windsor
Berkshire
SL4 1EP

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

United Kingdom

6283187001

4. Title of the invention

SALINE SOLUBLE INORGANIC FIBRES

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

PHILLIPS & LEIGH
7 Staple Inn
Holborn
London WC1V 7QF

Patents ADP number (if you know it)

0001289001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number
(if you know it)

Date of filing
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

Yes

- a) any applicant named in part 3 is not an inventor, or
 - b) there is an inventor who is not named as an applicant, or
 - c) any named applicant is a corporate body.
- See note (d))

Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form	-
Description	4
Claim(s)	1 <i>W</i>
Abstract	-
Drawing(s)	-

10. If you are also filing any of the following, state how many against each item.

Priority documents	-
Translations of priority documents	-
Statement of inventorship and right to grant of a patent (<i>Patents Form 7/77</i>)	To follow
Request for preliminary examination and search (<i>Patents Form 9/77</i>)	1
Request for substantive examination (<i>Patents Form 10/77</i>)	-
Any other documents (<i>please specify</i>)	-

11. I/We request the grant of a patent on the basis of this application.

Signature <i>J.C. Boff</i>	Date 21.06.96
PHILLIPS & LEIGH	

12. Name and daytime telephone number of person to contact in the United Kingdom
- | | |
|-----------|---------------|
| J.C. BOFF | 0171 405 0133 |
|-----------|---------------|

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

Notes

- If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.*
- Write your answers in capital letters using black ink or you may type them.*
- If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.*
- If you have answered 'Yes' Patents Form 7/77 will need to be filed.*
- Once you have filled in the form you must remember to sign and date it.*
- For details of the fee and ways to pay please contact the Patent Office.*

SALINE SOLUBLE INORGANIC FIBRES

This invention relates to saline soluble inorganic fibres.

Saline soluble inorganic fibres have been described in several patent specifications, see for example WO93/15028. Fibres are required to be soluble in saline solution so that inhaled or ingested fibres dissolve rather than providing a source of irritation or otherwise affecting health. WO93/15028 showed that fibres comprising SiO_2 , CaO and MgO and having a silica content of greater than 58% (or greater than 58% plus 0.5 times (10-MgO) if $\text{MgO} > 10\text{wt}\%$) had suitable shrinkage characteristics at 800°C and 1000°C to be usable as refractory materials. A further feature of WO93/15028 was the use of the percentage of non-bridging oxygens present to predict the solubility of fibres in physiological saline solution.

Various subsequent applications have described the effect of P_2O_5 and B_2O_3 on solubility - see for example WO95/29135. P_2O_5 is alleged to have a solubilising effect on such fibres.

The German government have proposed a fibre classification which turns on a variable K_1 which is defined as:

$$K_1 = \sum (\text{Na, K, B, Ca, Mg, Ba -oxide}) - 2 * \text{Al-oxide}$$

(the amounts of the oxides being expressed as weight %)

According to the proposed fibre classification if K_1 is greater than 40 the fibre concerned is deemed safe. If K_1 lies between 30 and 40 the fibre requires only minor health warnings to be made. If K_1 is less than 30 more serious marking is required. It is readily apparent that it is difficult to provide a high K_1 fibre ($K_1 > 40$) while still providing a refractory fibre like that of WO93/15028 ($\text{SiO}_2 > 58\text{wt}\%$), there being a very narrow window of compositions to meet.

As a result of investigating fibre compositions that may meet the fibre classification and yet still be refractory enough to meet the standard of WO93/15028 (shrinkage of less than 3.5% at both 800°C and 1000°C) the applicants have found that addition of P_2O_5 to compositions allows a broader range of refractory fibres to be produced than had previously been appreciated.

It appears that an important factor in determining the refractoriness of a fibre is the percentage of non-bridging oxygens. If this percentage is 61.4% or more (calculated on the basis of the amounts of the components SiO_2 , CaO, MgO,

P₂O₅, and B₂O₃) the fibres fail shrinkage tests at 800°C and 1000°C (failure being defined as a shrinkage of 3.5% or more).

Accordingly the present invention provides the use of P₂O₅ as a component to improve the refractoriness of inorganic fibres comprising SiO₂, and CaO and/or MgO, the inorganic fibres having a composition such that the percentage of non-bridging oxygens is less than 61.4%.

The invention further provides saline soluble inorganic fibres having a shrinkage of less than 3.5% when exposed to 1000°C for 24 hours and having a shrinkage of less than 3.5% when exposed to 800°C for 24 hours, comprising:-

SiO ₂	52 - <58wt% [52 - <58+0.5×(MgO-10)wt% if MgO > 10wt%]
CaO	22 - 40wt%
MgO	0 - 17.5wt%
MgO + CaO	< 42wt%
P ₂ O ₅	0.5 - 10wt%
B ₂ O ₃	0 - 2wt%

and in which the percentage of non-bridging oxygens calculated on the basis of the amounts of the above named components is less than 61.4%.

The percentage of non-bridging oxygens (%N.B.O.) is calculated by converting the weight percentages of SiO₂, CaO, MgO, P₂O₅, and B₂O₃ to molar amounts and inserting these amounts into the equation:-

$$\%N.B.O. = \frac{2 \times (CaO + MgO + P_2O_5 + B_2O_3)}{(2 \times SiO_2 + CaO + MgO + 5 \times P_2O_5 + 3 \times B_2O_3)} \times 100$$

The reason the amounts of CaO, MgO, P₂O₅, and B₂O₃ are doubled in the numerator to this equation is that each contributes two non-bridging oxygens. The reason terms are multiplied in the denominator to this equation is to reflect the number of oxygen atoms each molecular formula possesses.

Table 1 shows the results of shrinkage and solubility tests on compositions comprising SiO₂, CaO, MgO, P₂O₅, and B₂O₃ as main ingredients. It is clear that where the percentage of non-bridging oxygens calculated on the basis of the amounts of the above named components is greater than 61.4% (those fibres lying above line A of Table 1) the fibres fail the shrinkage tests, having shrinkages of greater than 3.5% at either or both of 800°C and 1000°C.

WO93/15028 stressed the importance of alumina content and the fibres lying between lines B and A of Table 1 show that alumina contents of greater than 1wt% are damaging to the shrinkage properties of fibres.

The applicants have also found that the combined amount of CaO and MgO is important. Those fibres lying between lines C and B have a combined CaO and MgO content of greater than 42wt% and also fail the shrinkage tests.

The fibres below line C have a percentage of non-bridging oxygens less than 61.4%, an alumina content of less than 1wt%, and a combined CaO and MgO content of less than 42wt%. All of these fibres pass the shrinkage tests. These fibres fall within the compositional ranges:-

SiO ₂	52.4 - 57.85wt%
CaO	22.2 - 39.4wt%
MgO	1.96 - 17.4wt%
P ₂ O ₅	0.82 - 7.8wt%
B ₂ O ₃	0 - 1.95wt%
Al ₂ O ₃	<1wt%

The solubility results presented in Table 1 were obtained by the methods described in WO93/15028 and show a high solubility for all of the fibres produced.

It can be seen that all of the fibres below line C have a K₁ of more than 35 and more than half have a K₁ of more than 40.

While the above description and the claims refer to P₂O₅, B₂O₃, SiO₂, CaO and MgO it will be clear to the person skilled in the art that the pure materials need not be used and that provision of these components in combined form (e.g. provision of P₂O₅ in the form of mixed oxide phosphates) is part of the invention.

Code	Chemical Composition (NRF - Weight percent)														Kl	Shrinkage		Solubility (ppm)			Total	CaO+MgO	% N.B.O.
	CaO	MgO	P2O5	SiO2	Al2O3	Na2O	K2O	B2O3	Fe2O3	ZrO2	SrO	800°C	1000°C	CaO		MgO	SiO2						
	Chemical Composition (NRF - Weight percent)																						
Code	CaO	MgO	P2O5	SiO2	Al2O3	Na2O	K2O	B2O3	Fe2O3	ZrO2	SrO	800°C	1000°C	CaO	MgO	SiO2	Total	CaO+MgO	% N.B.O.				
LTP																							
LTP 8	24.95	19.18	3.41	51.69	0.25	0.30	0.05		0.17	<0.05	<0.05	44.0	40.0	40.0	53	98	177	328	44.14	68.5%			
LTP 9	24.81	18.66	5.10	50.42	0.38	0.31	<0.05		0.17	0.15	<0.05	43.0	23.9	38.8	59	115	193	367	43.47	68.1%			
LTP11	25.13	19.07	2.51	52.54	0.28	0.25	0.05		0.17	<0.05	<0.05	43.9	46.8	39.1	55	94	174	323	44.20	68.0%			
LTP16	31.83	12.27	3.39	51.59	0.26	0.42	0.06		0.17	<0.05	<0.05	44.1	49.1		79	76	200	355	44.11	66.1%			
LTP10	24.48	17.89	2.48	54.46	0.21	0.28	0.05		0.16	<0.05	<0.05	42.3	3.62	19.1	58	90	169	317	42.37	64.7%			
LTP 4	24.04	17.78	3.31	53.85	0.31	0.26	0.05		0.15	0.25	<0.05	41.5	3.71	4.77	56	95	180	331	41.83	64.3%			
LTP 5	24.22	17.17	4.91	52.72	0.33	0.30	<0.05		0.14	0.21	<0.05	41.0	3.63	5.39	65	106	191	362	41.40	64.1%			
LTP17	38.39	5.54	3.41	51.22	0.40	0.42	0.07		0.16	0.38	<0.05	43.6	45.2	43.8	83	32	191	306	43.94	63.9%			
LTP23	38.62	5.56	2.57	52.23	0.34	0.46	0.07		0.15	<0.05	<0.05	44.0	42.90		82	29	199	310	44.18	63.7%			
LTP14	30.93	11.01	4.90	51.96	0.30	0.45	0.05		0.15	0.25	<0.05	41.8	3.24	3.92	78	69	191	338	41.95	63.0%			
LTP13	11.28	27.95	3.26	57.2	<0.05	0.13	<0.05		0.17	<0.05	<0.05	39.4	5.72	5.26	30	117	188	335	39.23	63.0%			
LTP12	30.93	11.35	3.36	53.52	0.32	0.31	0.06		0.15	<0.05	<0.05	42.0	2.55	30.1	82	72	207	361	42.27	62.6%			
LTP20	31.05	11.35	2.52	54.14	0.32	0.31	0.06		0.16	0.10	<0.05	42.1	3.38	29.7	85	71	200	356	42.40	62.6%			
LTP15	36.89	5.70	5.05	51.22	0.31	0.43	0.10		0.16	0.13	<0.05	42.5	3.41	5.03	88	35	204	327	42.59	62.2%			
LTP 3	22.89	16.69	6.70	52.58	0.25	0.29	<0.05		0.14	0.46	<0.05	39.4	23.3	29.5	43	166	141	350	39.58	61.9%			
LTP 7	10.37	27.85	3.29	58.18	<0.05	0.15	<0.05		0.16	<0.05	<0.05	38.4	10.9	15.5	36	132	152	320	38.23	61.4%			
LTP52	24.9	11.5	4.89	54.8	2.06	0.28	0.05	<0.05	1.38	<0.05	<0.05	32.6	32.1		72	74	140	286	36.40	56.0%			
LTP51	28.7	11	1.62	56.6	1.38	0.29	0.07	<0.05	0.26	<0.05	<0.05	37.3	3.07	3.61	82	69	159	310	39.70	58.4%			
LTP29	40.29	2.09	1.23	55.09	0.43	0.39	0.12		0.19	0.17	<0.05	42.0	45.9		76	10	206	292	42.38	58.8%			
LTP21	36.62	5.58	2.54	54.19	0.39	0.46	0.07		0.15	<0.05	<0.05	42.0		35.5	58	34	208	300	42.20	60.3%			
LTP30	39.40	1.96	2.22	55.25	0.45	0.41	0.10		0.21	<0.05	<0.05	41.0	1.74	2.04	72	11	209	292	41.36	57.5%			
LTP41	31.36	9.48	0.85	55.63	0.27	0.30	0.07	1.88	0.16	<0.05	<0.05	42.5	1.20	2.32	87	60	194	361	40.84	60.0%			
LTP 6	29.83	10.45	3.34	55.65	0.21	0.32	0.05		0.15	<0.05	<0.05	40.2	1.89	2.76	65	52	172	289	40.28	59.0%			
LTP34	30.44	9.81	1.68	57.3	0.25	0.31	0.07		0.15	<0.05	<0.05	40.1	1.40	1.79	76	51	188	315	40.25	58.0%			
LTP43	30.51	9.68	1.68	56.19	0.28	0.32	0.07	1.11	0.15	<0.05	<0.05	41.1	0.97	1.84	62	66	187	327	40.19	58.8%			
LTP42	30.55	9.56	0.86	57.13	0.27	0.33	0.07	1.08	0.15	<0.05	<0.05	41.1	1.04	1.81	75	65	192	344	40.12	58.2%			
LTP47	22.2	17.4	3.98	55.2	0.31	0.31	0.05	<0.05	0.11	<0.05	<0.05	39.3	1.97	2.14	58	104	197	359	39.60	61.0%			
LTP38	34.82	4.73	0.82	57.84	0.31	0.30	0.08	0.94	0.15	<0.05	<0.05	40.3	1.07	1.40	83	25	175	292	39.56	55.4%			
LTP 2	23.35	16.10	4.87	54.25	0.46	0.24	<0.05		0.16	0.58	<0.05	38.8	2.24	3.05	53	96	167	316	39.45	60.8%			
LTP39	34.35	4.73	1.67	57.39	0.27	0.30	0.08	1.06	0.14	<0.05	<0.05	40.0	1.47	1.93	32	33	203	284	39.08	55.2%			
LTP 1	23.29	15.66	3.33	57.01	0.24	0.22	0.06		0.14	<0.05	0.05	38.7	1.31	1.77	63	89	175	327	38.94	58.7%			
LTP48	32	6.87	7.8	52.4	0.52	0.34	0.05	<0.05	0.15	0.18	<0.05	38.2	1.24	1.53	84	48	205	337	38.87	57.7%			
LTP40	33.67	4.75	0.86	57.85	0.38	0.31	0.08	1.95	0.15	<0.05	<0.05	40.0	1.15	2.39	40	32	194	291	38.42	54.5%			
LTP26	33.69	4.56	3.73	56.95	0.36	0.43	0.06		0.14	0.07	<0.05	38.0	1.22	1.40	91	28	193	312	38.25	54.0%			
LTP27	28.91	9.33	3.66	57.32	0.22	0.36	0.05		0.14	<0.05	<0.05	38.2	0.99	1.16	67	48	173	288	38.24	55.5%			
LTP46	28.4	8.69	2.67	59	0.29	0.33	0.06	<0.05	0.13	<0.05	<0.05	36.9	0.91	0.99	71	46	175	292	37.09	53.3%			

CLAIMS

1. The use of P_2O_5 as a component to improve the refractoriness of inorganic fibres comprising SiO_2 , and CaO and/or MgO, to produce inorganic fibres having a composition such that the percentage of non-bridging oxygens is less than 61.4% and having a shrinkage of less than 3.5% when exposed to 1000°C for 24 hours and having a shrinkage of less than 3.5% when exposed to 800°C for 24 hours.
2. Saline soluble inorganic fibres having a shrinkage of less than 3.5% when exposed to 1000°C for 24 hours and having a shrinkage of less than 3.5% when exposed to 800°C for 24 hours, comprising:-

SiO_2	52 - <58wt% [52 - <58+0.5×(MgO-10)wt% if MgO > 10wt%]
CaO	22 - 40wt%
MgO	0 - 17.5wt%
MgO + CaO	< 42wt%
P_2O_5	0.5 - 10wt%
B_2O_3	0 - 2wt%

and in which the percentage of non-bridging oxygens calculated on the basis of the amounts of the above named components is less than 61.4%.

3. Saline soluble inorganic fibres as claimed in claim 2 in which the fibres have a composition:-

SiO_2	52.4 - 57.85wt%
CaO	22.2 - 39.4wt%
MgO	1.96 - 17.4wt%
P_2O_5	0.82 - 7.8wt%
B_2O_3	0 - 1.95wt%
Al_2O_3	<1wt%

PCT NO : 0897 / 01667

Form 2317 - 20.6.47

Agent : Enrique S. Leigh

THIS PAGE BLANK (USPTO)